



(1) Publication number:

0 686 707 A1

(P)

## **EUROPEAN PATENT APPLICATION**

- 21) Application number: 94108885.8
- (f) Int. Cl.6: C23C 16/02, C23C 30/00

- 2 Date of filing: 09.06.94
- ② Date of publication of application: 13.12.95 Bulletin 95/50
- Designated Contracting States:
   DE FR GB IT

- 7) Applicant: MITSUBISHI MATERIALS CORPORATION 5-1, Ohtemachi 1-chome Chiyoda-ku, Tokyo (JP)
- Inventor: Ooshika, Takatoshi, c/o Tukuba Plant Mitsubishi Materiais Corp., 1511, Ooazakomaki Ishige-cho, Yuuki-gun, Ibaragi-ken (JP)
- Representative: Müller-Boré & Partner Patentanwälte
  Grafinger Strasse 2
  D-81671 München (DE)

- Surface coated cutting tool
- (Object)

The invention relates to a cutting tool whose surface is coated with a composite hard layer formed by means of chemical vapor deposition and having excellent wear resistance and chipping resistance.

(Construction)

A cutting tool consists substantially of a substrate whose surface is coated with a composite hard layer consisting substantially of an inner layer including one or more layers of titanium carbide, titanium nitride, titanium carbonitride, titanium carbonitride, and an outer layer including at least one alumina layer. The alumina layer contains so much x-type alumina that an X-ray intensity ratio I<sub>A</sub>/I<sub>B</sub> of two specific crystal faces A and B in X-ray diffraction is not smaller than 2, where the A-face and B-face denote faces of x-type alumina defined as those whose interfacial distances are 2.79Å and 2.57Å in ASTM4-0878, and I<sub>A</sub> and I<sub>B</sub> denote X-ray intensity of the faces A and B in X-ray diffraction.

#### DETAILED DESCRIPTION OF THE INVENTION

[Field of industrial application]

The present invention relates to a surface coated cutting tool having excellent wear resistance and chipping resistance, the cutting tool including a cemented carbide substrate whose surface is coated with a composite hard layer formed by means of chemical vapor deposition, the composite hard layer consisting substantially of an inner layer including one or more layers of titanium carbide, titanium nitride, titanium carbonitride, titanium carbonitride, titanium carbonitride, and titanium oxicarbonitride (hereinafter referred to generally as titanium compound layers), and an outer layer including at least one alumina layer.

[Prior art]

35

For the purpose of continuous and interrupted cutting of steel, it has been well known practice to use a surface coated cutting tool including a cemented carbide substrate whose surface is coated with a composite hard layer formed by means of chemical vapor deposition, the composite hard layer consisting substantially of an inner layer including a titanium compound layer and an outer layer including at least one alumina layer.

The alumina layer is chemically stable and displays excellent face wear resistance, but it adheres poorly to the substrate and lacks toughness. Thus, the surface of the cemented carbide substrate is coated first with a titanium compound layer formed by means of chemical vapor deposition, then an alumina layer is formed on the titanium compound layer by means of chemical vapor deposition, thereby giving wear resistance and toughness to the formed composite hard layer to improve chipping resistance.

For the purpose of forming the alumina layer of the composite hard layer by means of chemical vapor deposition, a method is known for speeding up the growth rate of the alumina layer by using a reaction gas obtained by adding 0.01 to 1.0 vol % of hydrogen sulfide gas to the normal reaction gas.

The use of this method shortens the time during which the inner layer made of titanium compound and the cemented carbide substrate are held at high temperature, with the result that the structure of the inner layer and the substrate is unlikely to change. Thus, it is said that a surface coated cutting tool having a better performance than the conventional tools can be obtained according to this method (refer to, for example, Japanese Examined Patent Publication 62-3234).

The alumina layer obtained by using a reaction gas containing 0.01 to 1.0 vol % of hydrogen sulfide gas is mainly an  $\alpha$ -type alumina layer. It is also known that a  $\alpha$ -type alumina layer is obtainable by changing the volume of carbon dioxide gas in the reaction gas.

[Problems to be solved by the invention]

In recent years, there has been an increasing demand for a labor-saving and more rapid cutting operation. This demand strongly requires a high speed in continuous and interrupted cutting operation, that is both high speed feeding and high speed cutting under more severe conditions. During the high speed cutting operation, the temperature of the cutting edge rises above 1000°C and steel chips of exceedingly high temperature pass along the face of the cutting tool, which accelerates wear of the face. Thus, the cutting tool is chipped or damaged at a relatively early stage. Under these severe conditions, the cutting tools coated with the composite hard layer including the conventional alumina layer have a relatively short lifetime because the coated layer has insufficient wear resistance and chipping resistance.

[Means for solving the problem]

In view of the above, the inventors of the present invention carried out a research to develop a cutting tool whose surface is coated with a composite hard layer including an alumina layer having better wear resistance and chipping resistance than the prior art and obtained the following results.

A cutting tool comprising a substrate whose surface is coated with a composite hard layer consisting substantially of an inner layer including one or more layers of titanium compounds, and an outer layer including at least one alumina layer containing so much x-type alumina that an X-ray intensity ratio of two specific crystal faces in X-ray diffraction is not smaller than 2, has better wear resistance and chipping resistance than the conventional cutting tools coated with a composite hard layer including the conventional alumina layer.

The invention was developed on the basis of these research results and is directed to:

a cutting tool comprising a substrate whose surface is coated with a composite hard layer including an inner layer having one or more layers of titanium carbide, titanium nitride, titanium carbonitride, and an outer layer having at least one alumina layer, wherein the alumina layer contains so much x-type alumina that an X-ray intensity ratio I<sub>A</sub>/I<sub>B</sub> of two specific crystal faces A and B in X-ray diffraction is not smaller than 2, where the A-face and B-face denote faces of x-type alumina defined as those whose interfacial distances are 2.79Å and 2.57Å in ASTM4-0878, and I<sub>A</sub> and I<sub>B</sub> denote X-ray intensities of the faces A and B in X-ray diffraction.

The reason why the cutting tool according to the invention has better wear resistance and better chipping resistance compared with the conventional tools is thought to be that abnormal damage caused by friction between steel chips and the tool is unlikely to occur because x-type alumina, demonstrating orientation to the face A, makes the surface of the coated layer smooth.

Thus, when the alumina layer contains so much special *κ*-type alumina that the ratio of X-ray intensity I<sub>A</sub> of the face A to that I<sub>B</sub> of the face B in X-ray diffraction is not smaller than 2, i.e., I<sub>A</sub>/I<sub>B</sub> ≥ 2, wear resistance and chipping resistance are further improved. Thus, the cutting tool whose surface is coated with the composite hard layer including this alumina layer has a longer lifetime even under severe working conditions such as high speed cutting.

Besides special x-type crystals whose X-ray intensity ratio ( $I_x/I_B$ ) is not smaller than 2, the alumina layer according to the invention may contain alumina having a different crystallo-graphic structure. However, it is desirable that the amount of special x-type crystals in the alumina layer be at least not less than 30 %, preferably not less than 50 %, and most preferably not less than 70 %. The percentage of special x-type crystals is obtained from the following equation:

Percentage of special κ-type crystals =

sum of counts of all the peaks of  $\kappa \cdot Al_2O_3$  in X-ray diffraction

x 100

sum of counts of all the peaks of Al<sub>2</sub>O<sub>3</sub> in X-ray diffraction

It is not necessary for the alumina layer to be an outer-most layer. At least one layer of titanium compound may be formed on the alumina layer.

A method for forming the inventive alumina layer containing special x-type crystals whose peak intensity ratio  $(I_A/I_B)$  is not smaller than 2 is as follows.

During an alumina coating reaction, a substrate coated with titanium compounds is held in a mixed gas containing no CO<sub>2</sub> gas, but AlCl<sub>3</sub>, H<sub>2</sub> and, if necessary, HCl for a predetermined time in the first step, and is subsequently caused to react in a mixed gas containing CO<sub>2</sub>, AlCl<sub>3</sub>, H<sub>2</sub> and, if necessary, HCl in the second step.

It will be appreciated that the mixed gas used for the coating reaction may further contain H2S if necessary.

The conditions for the alumina coating reaction are described in detail below:

First Step -

25

30

Temp.: 800 to 1050 °C, Time: 1 to 120 min.

Gas Composition: 0.5 to 20 vol % of AlCl<sub>3</sub>, 0 to 20 vol % of HCl, remainder H<sub>2</sub>

Second Step -

Temp.: 800 to 1050 °C

Gas Composition : 0.5 to 30 vol % of  $CO_2$ , 0.5 to 20 vol % of  $AICI_3$ , 0 to 20 vol % of HCI, remainder  $H_2$  If necessary, 0.01 to 5 vol % of  $H_2S$  may be added at the beginning or in the middle of the second step. The composition of the mixed gas may be changed continuously during the transition from the first step to the second step.

## [Example]

The surface coated cutting tool according to the invention will be described in more detail by way of an example.

A mixed powder having the composition: 87%WC-2%TiC-1%TiN-4%TaC-6%Co was prepared according to a normal method. The mixed powder prepared in this way was compressed into a green compact, which was then sintered at a temperature of 1410 or in vacuum for 1 hour. In this way, a cemented carbide substrate A of the form of ISO SNMG120408 was prepared.

Similarly, a mixed powder having the composition: 82%WC-5%TiC-5%TaC-8%Co was prepared according to a normal method. The mixed powder prepared in this way was compressed into a green compact, which was then sintered at a temperature of 1380° in vacuum for 1 hour. In this way, a cemented carbide substrate B of the form of ISO SNMG120408 was prepared.

On the surface of the cemented carbide substrate A, there was a tough surface layer of a thickness of 20 µm including substantially no hard disperse phase (Ti, Ta, W) (C, N) and having a Co-amount increased to a maximum of 1.8 times greater than the internal Co-amount. On the other hand, there was almost no difference in structure between the surface and internal portions of the cemented carbide substrate B.

Honing of as large as 0.05R (R is the radius of the edge of the cutting tool in mm) was applied to the cutting edges of the thus obtained cemented carbide substrates A and B, and the surfaces of the substrates were washed. The inventive surface coated cutting tools 1 to 8 were manufactured by coating the surface of the substrate A under the conditions specified in TABLE-1 to TABLE-7 and by coating the surface of the substrate B under the conditions specified in TABLE-8. For the purpose of comparison, the conventional surface coated cutting tools 1 to 8 were manufactured by coating the surface of the substrate A under the conditions specified in TABLE-9 to TABLE-15 and by coating the surface of the substrate B under the conditions specified in TABLE-16.

X-ray diffraction was conducted for the inventive cutting tools 1 to 8 and the conventional cutting tools 1 to 8 to measure the X-ray intensity ratio I<sub>A</sub>I<sub>B</sub>. The measurement results are shown in TABLE-17.

Further, a continuous cutting test and an interrupted cutting test were conducted for the above cutting tools under the following conditions. A wear width on the flank face was measured in the former test, whereas the lapse of time until chipping was measured in the latter test. The measurement results in the respective tests are again shown in TABLE-17.

### [Cutting Test Conditions]

3	ıĸ	
·	•	

40

- Continuous Cu	itting -
Work piece Cutting speed Feed rate Cutting depth Cutting time Coolant	JIS SCM440 (hardness : H <sub>B</sub> 220) round bar 250 m/min. 0.3 mm/rev. 1.5 mm 20 min. none

45

- Interrupted Cutt	ing -
Work piece JIS Cutting speed Feed rate Cutting depth Cutting time Coolant	SNCM439 (hardness: H <sub>B</sub> 280) rectangular bar 100 m/min. 0.236 mm/rev. 3.0 mm 30 min. none

50

TABLE-18, the ASTM table, defines faces by means of face index [indicated in (h, k, l)], but the specific faces of this x-Al<sub>2</sub>O<sub>3</sub> are not yet identified. "Face A" and "face B" have been written in a blank column of this table in order to identify the faces. Fig. 1 is a graph showing X-ray diffraction data of the coating layer of the inventive cutting tool 5 in the example. I<sub>A</sub> and I<sub>B</sub> represent x-ray intensities of the faces A and B. A

## EP 0 686 707 A1

theoretical d-value of the face A is 2.79 according to TABLE-18, but a measured d-value thereof is 2.812 which varies slightly from the theoretical d-value. The theoretical and measured d-values of the face B are 2.57 and 2.576, respectively. The horizontal axis of Fig. 1 represents 20 which is an angle (in degree) an X-ray makes in the X-ray diffraction. Numerical values (2.812, 2.576, etc.) written on the respective peaks in this graph denote an interfacial distance d (in Å).

							lst STEP	2nd	STEP	_				
10			H,	REM.	REM.	REM.	REM.	REM.	REM.	(REM. denotes remainder)				
15			H <sub>1</sub> S						6.0	es rem				
		NOL *	ő					4	4	denot				
20		rion (	Alcı,				3	7	2	(REM.				
		OMPOS	8			г								
25	TIONS	GAS CO	z,	25	25	23								
	CONDITIONS	REACTION GAS COMPOSITION (VOL %)	9		9.0									
30		8	f			н					•			
35 T-8788E			ricı,	7	77	2							ſ	
		TIME	(MIN)				οτ	οτ	120			_[		
40	REACTION	PRES- SURE	(Torr)	20	20	20	20	05	90					
<b>4</b> 5		REAC.	()	910	910	1010	0101	0101	0101					
50		THICK- NESS	(m#)	0.2	9.0	0.5	2.0	2.0	2.0		ıyer	ıyer	ıyer	Base Material
		TYPE	LAYER	Tin	TiQ	Ticno		\$1.9		<b></b>	3rd La	2nd Layer	1st Layer	Base N
55		LAYER		18t	2nd	3rd		4th						•

								1st STEP	2nd	STEP						
5				н,	REM.	REM.	REM.	REM.	REM.	REM.	REM.	inder)				
10				H <sub>2</sub> S						0.3		в геша				
70			* Ton	ર્ક					4	4		enote				
15			REACTION GAS COMPOSITION (VOL %)	Alcı,				y	5	В		(REM. denotes remainder)				
			OMPOS	8			1									
20		TIONS	SAS CA	z,	25	25	1.5				70					
		CONDITIONS	ACTION (	£,		0.6										
26			RE	ŧ			н									
	TABLE-2			Ticl,	7	n	7				1				[	
30		NOI	TIME	(MIN)				10	10	120						
35		REACTION	PRES- SURE	(Torr)	20	50	80	05	05	90	300					
40			REAC. TEMP.	(၃)	900	900	1010	1010	0101	1010	006					
			THICK-	(w#)	0.2	0.6	0.5	2.0	2.0	2.0	0.5		yer	yer	yer	Base Material
45			TYPE	LAYER	TIN	Tick	Ticno		A1.0,		TÍN		3rd Layer	2nd Layer	1st Layer	Base M
50			LAYER		18t	2nd	3rd		4th		Sth					

							1st STEP	2nd	STEP					
6			H,	REM.	REM.	REM.	RBM.	REM.	REM.	inder)				
10			H,S		!				0.2	в геша				
		VOL *	8					10	10	denote				
15		REACTION GAS COMPOSITION (VOL %)	Alcı,				е	E	ю	(REM. denotes remainder)				
		OMPOS	8			1								
20	CONDITIONS	GAS C	ž	57	32	25								
	CONDI	ACTION	CH, CN		8.0									
26		2	£			1								
TABLE-3			ricı,	m	77	£							ſ	
30	rion	TIME	(MIN)				20	30	300		1			
35	REACTION	PRES- SURE	(Torr)	120	50	100	20	20	20					
40		REAC.	(00)	906	006	1020	980	086	086					
		THICK- NESS	(w#)	0.5	6.0	0.5	6.0	6.0	0.9		ıyer	ıyer	ıyer	Bage Material
<b>4</b> 5		TYPE	LAYBR	Tin	Tick	Ticno		,0°.			3rd Layer	2nd Lay	1st Layer	Ваве 1
50		LAYER		18t	2nd	3rd		4ch						٠.

						,		lst STEP	2nd	STEP						
5				H,	REM.	REM.	REM.	REM.	REM.	REM.	REM.	nder)				
40				H,S						0.2		remai				
10			VOL *	83					10	15		notes				
15			REACTION GAS COMPOSITION (VOL 1)	MC1,				4	4	7		(REM. denotes remainder)				
			OMPOS	8			1									
20		TIONS	GAS O	Σ.	57	32	25				20					
		CONDITIONS	ACTION	E E		9.0	<b>!</b>									
25			RE	ŧ			1									
•	TABLB-4			ricı,	E	7	e .				1				ľ	
30	F.	NOI.	TIMB	(MIN)				20	30	300						
35		REACTION	PRES- SURE	(Torr)	120	20	100	20	50	05	300					
40			REAC. TEMP.	ົບ	920	920	980	980	980	980	006					
			THICK-	(ma)	5.0	6.0	5.0	0.9	0.9	0.9	5.0		ıyer	ıyer	ıyer	Base Material
<b>45</b>			TYPE	LAYER	Tin	Tick	Ticho		A1,0,		Tin		3rd Layer	2nd Layer	1st Layer	Base N
50			LAYER		18t	2nd	3rd		4th		5th					

			-				1st STEP	2nd	STEP
5					#	REM.	REM.	REM.	REM.
10					H <sub>2</sub> S				0.5
			VOL		8			4	7
15			REACTION GAS COMPOSITION (VOL 1)		MCI,		S	7	2
			OMPOS		8				
20		TIONS	SAS C		ž	32			
		CONDITIONS	ACTION		CH, CH	8.0			
26			22		ฮ์				
	Table-5				ricı	2			
30		LION	TIME		(MIN)		20	30	300
35		REACTION	PRES-	SURE	(Torr)	95	05	05	05
40			REAC.	TEMP.	(0.)	670	066	066	066
	:		THICK-	NESS	(w#)	6.0	6.0	6.0	6.0
<b>45</b>			TYPE	OF	LAYER	TICN		A1,0,	
50	-			LAYER	-	18t	,	2nd	

55

2nd Layer	1st Layer	Base Material

(REM. denotes remainder)

9

						lst STEP	2nd	STEP					
i			H,	REM.	REM.	REM.	REM.	REM.	nder)				
		_	B,S					0.2	remai				
		VOL *)	දි				10	10	notes				
		REACTION GAS COMPOSITION (VOL %)	Alcı,			1	2	3	(REM. denotes remainder)				
		OMPOS	8										
	TIONS	GAS O	ž		36								
	CONDITIONS	ACT ION	<b>B</b> , <b>B</b>										
		REJ	ਰੱ	6	7						•		
TABLE-6			ric1,	E.	в								
•	rion	TIME	(MIM)			96	30	300					
	REACTION	PRES- SURB	(Torr)	20	05	05	05	50					
		REAC. TEMP.	ပ္	1020	1000	096	096	096					
	!	THICK- NESS	(m4)	ο·ε	3.0	0.9	6.0	6.0		ıyer	ıyer	yer	Base Material
			LAYER	Tic	Ticn		A1,0,			3rd Layer	2nd Layer	1st Layer	Base M
		LAYER		lst	2nd		3rd						

							1st STEP	2nd	STEP						
5				н	REM.	REM.	REM.	REM.	REM.	REM.	inder)				
10				H,S					0.1		s rema				
			VOL *	65				10	10		lenote				
15			REACTION GAS COMPOSITION (VOL %)	Alcı,			е	е	9		(REM. denotes remainder)				
			OMPOS	8											
20		CONDITIONS	ଜୟ ପ	ν,		26				55					
		CONDI	ACTION	£,											
25			REJ	ŧ	6	7									
	TABLE-7			Ticl,	m	m	:			1				[	
30	•	NOI	TIMB	(MIN)			30	30	300						
35		REACTION	PRES- SURE	(Torr)	20	20	20	90	05	300					
40			REAC. TEMP.	() မ	1020	1000	096	950	056	900					
			THICK- NESS	(ma)	3.0	3.0	6.0	0.9	0.9	0.5		ıyer	ıyer	ıyer	Base Material
<b>45</b>			TYPE	LAYER	Tic	Tick		A1,0,		TİN		3rd Layer	2nd Layer	1st Layer	Base N
50			LAYER		18t	2nd		3rd		4th					•

						1st STEP	2nd STEP				
				H,	REM.	REM.	REM.	nder)			
				H,S			0.05	s remai			
		OL ()		8			7	enote			
		REACTION GAS COMPOSITION (VOL 1)		Alcı,		9	٥	(REM. denotes remainder)			
		OMPOS1		8							
	TIONS	SAS CC		z.	26						
	CONDITIONS	ACTION (		CH, CH							
		22		ŧ	7						•
TABLE-8				ਜ਼ਹ,	9						
r	NOI.	TIME		(MIN)		20	360				
	REACTION	PRES-	SURE	(Torr)	20	50	90				
		REAC.	TEMP.	(o.)	1020	930	930				
		THICK-	NESS	(w#)	5.0	6.0	6.0		ıyer	ıyer	Base Material
		TYPB	90	LAYER	Tich		A1,0,		2nd Layer	1st Layer	Base N
			LAYER		1st		2nd				

6					H,	REM.	REM.	REM.	REM.	ider)				
			_		H,S				0.3	remair				
10			VOL *		303				4	otes				
			ITION (		AlCl,				9	(REM. denotes remainder)				
15			MPOS		ខ			1						
		rions	D SAE		N N	35	25	23						
20		CONDITIONS	REACTION GAS COMPOSITION (VOL &)		GH,GR		9.0							
			RE		ŧ			τ						
26	TABLE-9				ricı,	7	7	8					ſ	
30	1	TON	TIME		(MIN)				120		ı			
35		REACTION	-SBRG	SURE	(Torr)	20	05	05	50					
_			REAC.	TEMP.	(î •)	910	910	1010	1020					
40			THICK-	NESS	(m <sub>4</sub> )	0.2	9.0	0.5	2.0		ıyer	ıyer	ıyer	Base Material
45			TYPB	OF	LAYER	Tin	Tick	Ticno	A1,0,		3rd Layer	2nd Layer	1st Layer	Base M
50				AYER		1st	2nd	3rd	4th					

					В,	REM.	REM.	REM.	REM.	REM.	inder				
5					H <sub>2</sub> S	щ	μ,	-	0.3 F		rema				
10			( <b>)</b> 10		СО, Н				4		enotes				
70			ION (VC		Alcı,				7		(REM. denotes remainder				
15	`		POSIT		8			1							
		IONS	AS CO		N,	25	20	23		55					
20		CONDITIONS	REACTION GAS COMPOSITION (VOL *)		G, G		9.0		·						
		!	REA		ฮ์			1				•			
25	TABLE-10				ricı,	7	77	7		1				ſ	
30	H	NO	TIME		(MIN)				120						
35		REACTION	PRES-	SURE	(Torr)	90	20	20	50	300					
			REAC.	TEMP.	(၁.)	900	900	1010	1020	900					
40			THICK-	NBSS	(m 4)	0.2	0.6	0.5	2.0	0.5		yer	yer	yer	Base Material
45			TYPE	OF	LAYER	Tin	Ticn	Ticno	A1,0,	TIN		3rd Layer	2nd Layer	1st Layer	Bage M
50				LAYER		18t	2nd	3rd	4th	Sth					

				н,	REM.	REM.	REM.	REM.	inder			
6				H,S		-	_	0.2	э гета			
			OF (\$)	60				10 0	lenotes			
10			REACTION GAS COMPOSITION (VOL %)	Alcı,				3	(REM. denotes remainder)			
15	,		POSITI	8			1					
15		SNC	S COM	ž,	57	32	25					
		CONDITIONS	N GAS		1							
20		CON	ACTIC	GH, CA		9.						•
	4		RE	Ħ.			п					
26	TABLE-11			ricı,	3	7	ю					ſ
30	<b>H</b>	ION	TIME	(MIN)				300		_		
	,	REACTION	PRES- SURE	(Torr)	120	50	100	50				
35			REAC.		006	006	1020	1000				
40			THICK- 1		0.5	6.0	0.5	6.0		er	rer	er
<b>4</b> 5			TYPE	AX XX	TIN	Tick	Ticno	A1,0,		3rd Layer	2nd Layer	1st Layer
50			LAYBR		lst	2nd	3rd	4th				

55

15

Base Material

5			70L %)		
15		CONDITIONS	REACTION GAS COMPOSITION (VOL %)		
26	TABLE-12	COND	REACTION		
30	r'	NOI	TIME		(MIM)
35		REACTION	PRES-	SURE	(Torr)
40			REAC.	TEMP.	(၁.)
••			THICK-	NESS	
15			TYPE	OF	LAYER (µm)
	]			~	

55

	_	-		<del></del>		1		7
			н	REM.	REM.	REM.	REM.	REM.
			H,S				0.2	
	VOL *		કે				10	
	ITION (		Alcı,				3	
	MPOS		8			ī		
SNOT	AS CO		Z,	22	32	25		55
CONDITIONS	REACTION GAS COMPOSITION (VOL %)		GH, CR		0.8			
	REI		ŧ			1		
			Tici,	æ	2	3		1
NOT	TIME		(MIN)					
KEAC I TON	PRES-	SURB	(Torr)	120	05	100	05	300
	REAC.	TEMP.	(D.)	026	920	0001	1000	006
	THICK-	NESS	(m#)	5.0	6.0	0.5	6.0	0.5
	TYPE	90	LAYER	Tin	Ticn	Ticno	A1,0,	Tin
		LAYER		18t	2nd	3rd	4th	Sth

3rd Layer	2nd Layer	1st Layer	Base Material

(REM. denotes remainder)

					Y			เก		
					т.	REM.	REM.	(REM. denotes remainder)		
6					H,S	:	0.5	tes re		
10			VOL (*)		8		7	. deno		
			NOIT:		Alcı,		п	(REM		
15			MPOS1		8					
	: :	rions	DO SAE		ž	32				
20	:	CONDITIONS	REACTION GAS COMPOSITION (VOL 1)		g. G	8.0				
	Ħ		NE NE		ŧ					
26	TABLE-13				ric1,	8	:			
30		NOI	TIME		(MIN)		300			· · · ·
35		REACTION	PRES-	SURE	(Torr)	50	20		:	
			REAC.	TEMP.	(D.)	870	1020			
40			THICK-	NESS	(µm)	6.0	0.9		ıyer	707
45			TYPE	OP	LAYER	Ticn	A1,0,		2nd Layer	Tayer Taker
50				LAYER		1st	2nd			

55

17

Base Material

(REM. denotes remainder)

5		
10		
15		ONG
20		SWOTTTONOO
25	TABLE-14	
30		XCT-FORBO
35		
40		
45		

50

55

		H <sub>2</sub>	REM.	REM.	REM.
		H <sub>2</sub> S			10 0.2
	VOL *	8			10
	REACTION GAS COMPOSITION (VOL %)	co Alcl, co,			e
	SOAWC	8			
LIONS	ias cc	N <sub>3</sub>		56	
CONDITIONS	ACTION O	CH, CH,CN N,			
	<u>a</u>	Ë	6	4	
		ricı,	3	3	
NOI	TIMB	(MIN)			300
REACTION	PRES- SURB	(Torr)	05	05	05
	REAC. TEMP.	(oc)	1020	1000	1000
	THICK-	(µm)	3.0	3.0	0.9
:	TYPE	LAYER	Tic	Ticn	A1,0,
	LAYER		1st	2nd	3rd

2nd Layer
2nd Layer
1st Layer
Base Material

					H,	REM.	REM.	REM.	REM.	der)				
6						2	12		22	ะคลไท				
			٥		H <sub>2</sub> S			9*0		es re				
10	:		VOL &		<b>6</b> 0			10		lenot				
			REACTION GAS COMPOSITION (VOL &)		Alcı,			8		(REM. denotes remainder)				
15			MPOS		8									
		CONDITIONS	GAS CC		N,		26		55					
20		СОМВІ	ACTION		CH, CN		:							
	1		RE	,	ð	0	7						•	
25	TABLE-15				ਸ਼ਹ,	3	3		1					_
30		TION	TIMB		(MIN)			300			ı			
35		REACTION	PRES- SURE		(Torr)	20	20	20	300					
		<u>.</u>	REAC. TEMP.		(ົບ • )	1020	1000	066	006					
40			THICK- NESS		(#m)	3.0	3.0	6.0	0.5		ıyer	ıyer	ıyer	Material
45			TYPE		LAYER	ric	TICN	A1,0,	Tin		3rd Layer	2nd Layer	1st Layer	Base M
50	!		LAYER			18t	2nd	3rd	4th					

5		
10		
15		
20		
25		TABLE-16
30		TAB
35		
40		
45		

55

		 <del></del>		_   +
			H H	H <sub>2</sub>
			H,S	H <sub>2</sub> S
	VOL *		ဗ	Ś
	) NOILI		co Alcı, co, H.s	Alcı,
	MPOS		8	8
LIONS	SAS CC		N <sub>2</sub>	M <sub>2</sub>
CONDITIONS	REACTION GAS COMPOSITION (VOL %)		Ticl, CH, CH, N,	CH, CN
	REJ		ŧ	£ '
			rici,	ricı,
TION	TIME		(MIN)	(MIN)
REACTION	PRES-	SURE	SURE (Torr)	SURE (Torr) 50
	REAC.	TEMP.	TEMP.	TEMP. (°C) 1020
	THICK-	NESS	NESS (μm)	NESS (μm)
	TYPE	90	OF LAYER	
		LAYER	LAYER	LAYER 1st

2nd Layer	1st Layer	Dage Meterie

(REM. denotes remainder)

35		I,/I, R.	1 8	2 7	3 30	4 25	5 12	9 9	7 5	8 2	1 0.7	2 0.7	3 0.9	4 0.9	5 0.2	9.0	7 0.5	8 0.7
25 30	TABI	RATIO (%) WHERE I <sub>A</sub> /I <sub>B</sub> ≥ 2	95	95	100	100	100	90	90	100	• 0	0	0	0	0	0	0	0
15	TABLE-17	FLANK WEAR WIDTH (mm) AFTER 20 MIN. CONTINUOUS CUTTING TEST	0.21	0.20	0.18	0.20	0.24	0.27	0.26	0.31	0.44	0.43	0.51	0.54	0.49	0.53	0.50	0.62
6		LAPSE OF TIME UNTIL CHIPPING IN INTER- RUPTED CUTTING TEST (MIN.)	10.1	8.3	8.9	8.8	7.2	7.9	8.5	7.0	5.3	5.5	5.0	5.1	4.0	5.2	5.8	2.1

\* This ratio is set to 0 since the conventional surface coated cutting tools contain no special  $\kappa$ -type Al<sub>2</sub>O<sub>3</sub> of I<sub>A</sub>/I<sub>B</sub> > 2, though containing normal  $\kappa$ -type Al<sub>2</sub>O<sub>3</sub> of I<sub>A</sub>/I<sub>B</sub> < 2.

	ſ	<del></del>		ŀ							•										-			-,				7	faces			
5	٠		рķī																									of the				
o		COMINA	k-al <sub>2</sub> 0, Kappa alomina			K-Al <sub>2</sub> O <sub>3</sub> KAPPA ALUMINA			30	30	80	100	30																			d-values of the faces be assumed to be faces
5		4-A1 <sub>2</sub> 0,							K-Al <sub>2</sub> O, KAPPA A			1.49	1.45	1.43	1.39	1.34																
•			XIDB	1341						Face A	•	Face B																	ace B : de varied v			
)			Kappa aluminum oxidb	I/I,		30	20	10	40	9	20	80	30	40	70	10	80	30	40	50	60	30	90	9	70				. 2.79Å, F ed by those			
i	81	r-A1,0,	Kappa a	φp		6.2	2.4	4.2	3.04	2.79	2.70	2.57	2.41	2.32	2.26	2.16	2.11	2.06	1.99	1.95	1.87	1.82	1.74	1.64	1.54				ces define			
)	TABLE-18	6.2	30		Yes		٠,		-1403									1	argu					אב טייייי			USING		follows: Fa even the fa			
i		2.11	80		Filler	Coll.	d corr.abs.?		AL., IND. END. CHEM. 42 1398-1403			,	·	υ .						coror				MI 700001 TR GIOU : Common amagneticam anticata sincis	T TW WOOD T		IN 1960,		faces specified in ASTM as follows: Face A : $d = 2.79Å$ , Face B : $d = 2.57Å$ . d-values of the faces due to a lattice defect, but even the faces defined by those varied values may be assumed to be faces			
)		2.57	80		λ 1.5405	off			ND. END. C			•		ບໍ່.	N									TOW CON	died des		REVISED BY STUMPF		specifica a lattice			
į		1.39	100		λ 1.	Cut off								ບຸ				•	H	<b>E</b>				and the same	NA IKIBIUK		LUES REVIS	STANDARD.	are faces ary due to			
)	ASTM 4-0878	p	1/1,		Rad. CuKa	Dia. 144MM	I/I, VISUAL	•	Ref. STUMPP ET	(1950)			Sys.			Ref.		,		2V D	Ref.				ALPHA ALUMI	ROOM AIR.	D- AND I-VALUES	CORUNDUM AS STANDARD.	Faces A and B are A and B may vary o			

55 [Effect of the Invention]

As is clear from the results shown in TABLE-17, the value of  $I_A/I_B$  of x-type alumina of any of the inventive cutting tools 1 to 8 is not smaller than 2. On the contrary, the value of  $I_A/I_B$  of x-type alumina of

#### EP 0 686 707 A1

any of the conventional cutting tools 1 to 8 is smaller than 2. Further, any of the inventive cutting tools 1 to 8 demonstrates a smaller wear width on the flank face in the continuous cutting test and has a longer lapse of time until chipping in the interrupted cutting test, compared with the conventional cutting tools 1 to 8.

Thus, the surface coated cutting tool according to the invention has a better performance than the conventional tools, and the use thereof leads to a reduced frequency of replacement, thereby contributing greatly to development of industries.

#### Claims

15

30

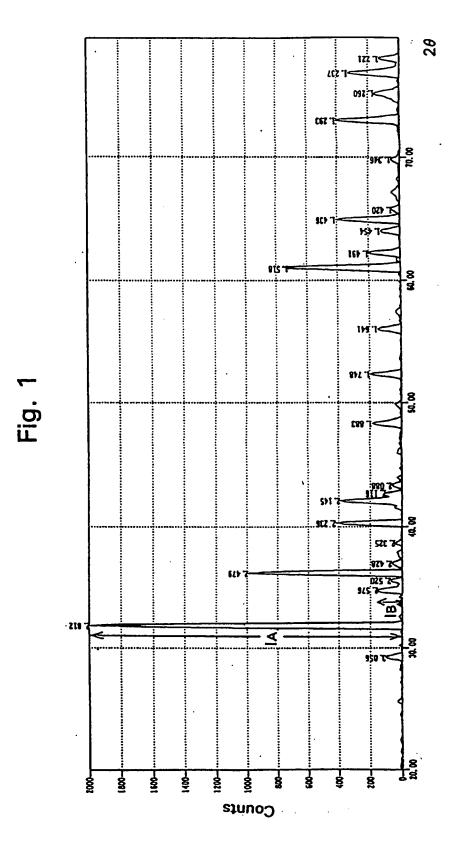
35

1. A cutting tool comprising a substrate whose surface is coated with a composite hard layer including an inner layer having one or more layers of titanium carbide, titanium nitride, titanium carbonitride, titanium carboxide, and titanium oxicarbonitride, and an outer layer having at least one alumina layer,

wherein the alumina layer contains so much x-type alumina that an X-ray intensity ratio  $I_A/I_B$  of two specific crystal faces A and B in X-ray diffraction is not smaller than 2, where the faces A and B denote faces of x-type alumina defined as those whose interfacial distances are 2.79Å and 2.57Å in ASTM4-0878, and  $I_A$  and  $I_B$  denote X-ray intensities of the faces A and B in X-ray diffraction.

- 2. A cutting tool according to claim 1, wherein the alumina layer contains at least 30 % of x-type alumina.
- 3. A cutting tool according to claim 2, wherein the alumina layer contains at least 50 % of x-type alumina.
  - 4. A cutting tool according to claim 3, wherein the alumina layer contains at least 70 % of x-type alumina.
- 5. A cutting tool according to claim 1, wherein the alumina layer containing x-type alumina is the uppermost layer.
  - 6. A process for producing a cutting tool according to claim 1 by coating the surface of a substrate with a composite hard layer including an inner layer having one or more layers of titanium carbide, titanium nitride, titanium carbonitride, titanium carbonitride, and titanium oxicarbonitride and an outer layer having at least one alumina layer, wherein the substrate coated with titanium compounds is held in a mixed gas containing no CO<sub>2</sub> gas but AlCl<sub>3</sub>, H<sub>2</sub> and, if necessary, HCl for a predetermined time in the first step and is subsequently caused to react in a mixed gas containing CO<sub>2</sub>, AlCl<sub>3</sub>, H<sub>2</sub> and, if necessary, HCl in the second step so that an alumina layer containing so much x-type alumina, that an X-ray intensity ratio I<sub>A</sub>/I<sub>B</sub> of two specific crystal faces A and B in X-ray diffraction is not smaller than 2, is produced, where the faces A and B denote faces of x-type alumina defined as those whose interfacial distances are 2.79Å and 2.57Å in ASTM4-0878 and I<sub>A</sub> and I<sub>B</sub> denote X-ray intensities of the faces A and B in X-ray diffraction.
- A process according to claim 6 characterized in that the mixed gas used for the coating reaction further contains H<sub>2</sub>S.
  - 8. A process according to claim 6 characterized in that the conditions for the alumina coating reactions in the first step are a temperature of 800 to 1050 °C, a time of 1 to 120 minutes, a gas composition of 0.5 to 20 vol % of AlCl<sub>3</sub>, 0 to 20 vol % of HCl, remainder H<sub>2</sub> and in the second step a temperature of 800 to 1050 °C and gas composition of 0.5 to 30 vol % of CO<sub>2</sub>, 0.5 to 20 vol % of AlCl<sub>3</sub>, 0 to 20 vol % of HCl, remainder H<sub>2</sub>.
  - A process according to claim 8 wherein 0.01 to 5 vol % of H₂S have been added at the beginning or in the middle of the second step.
  - 10. A process according to claim 8 wherein the composition of the mixed gas is changed continuously during the transition from the first step to the second step.

55



## **EUROPEAN SEARCH REPORT**

Application Number EP 94 10 8885

		DERED TO BE RELEVAN		G 100770170N 00777							
Category	Citation of document with in of relevant pas		Relevant to claim	CLASSIFICATION OF THE APPLICATION (bs.Cl.6)							
X	- 143, ISSN 0040-609 Vuorinen S et al 'Pl chemically vapour-de -alumina'	14, NR. 2, PAGE(S) 132 90 hase transformation in	1-5	C23C16/02 C23C30/00							
X	EP-A-0 408 535 (SEC 1991 * column 5, line 6	0 TOOLS AB ) 16 January - line 15 *	1-5								
X	EP-A-0 120 632 (GEN 1984 * example 1 *	ELECTRIC ) 3 October	6,8								
X	EP-A-0 083 842 (GEN 1983 * example 1 *	ELECTRIC ) 20 July	6,8	TECHNICAL FIELDS							
A,D	EP-A-0 045 291 (SAN 1982 * example 1 *	DVIK AB ) 3 February	7,9	SEARCHED (Int.CL.6)							
A	DE-A-36 33 986 (SCH June 1987 * claims 9,14 *	MALKALDEN WERKZEUG ) 25	10								
<b>A</b>	PATENT ABSTRACTS OF vol. 013, no. 466 ( & JP-A-01 180 980 ( 18 July 1989 * abstract *	JAPAN C-646) 20 October 1989 DAIJIETSUTO KOGYO KK)	1-10								
	The present search report has b	ocn drawa up for all claims									
	Place of sourch	Date of completion of the march		Exerciser							
X:pa Y:pa	THE HAGUE  CATEGORY OF CITED DOCUME  articularly relevant if taken alone articularly relevant if combined with an  comment of the same category	E : earlier patent di after the filing	ple underlying to comment, but purists in the applicati	hiished on, or on							
A : te	ocurrent of the same category choological background on-witten disclosure term ellate document	***************************************	L: document cited for other reasons  A: member of the same patent family, corresponding document								



# EUROPEAN SEARCH REPORT

Application Number EP 94 10 8885

	DOCUMENTS CONSID	ERED TO BE RELEVAN	T	]
Category	Citation of document with indi of relevant passa		Relevant to claim	CLASSIFICATION OF THE APPLICATION (IntCL6)
E	DATABASE WPI Section Ch, Week 9432 Derwent Publications Class LO2, AN 94-2598 & JP-A-6 190 605 (MI CORP) 12 July 1994 * abstract *	2, Ltd., London, GB; 393	1	
				TECHNICAL FIELDS SEARCHED (Int.CL6)
•				
	The present search report has be	en drawa up for all claims	7	
	Place of search	Date of completion of the nearth		Dominer .
1	THE HAGUE	7 November 1994	E	chult, H
A:te	CATEGORY OF CITED DOCUMEN urticularly relevant if taken alone articularly relevant if combined with anot ocus act of the same category schoological background co-written disclosure termediate document	E : earlier patent after the fillin her D : document cite L : document cite	document, but pr g date of in the applicat d for other reason	ablished on, or ion